

PCT

WORLD INTELLECTUAL PRO
International



INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606125A1

(51) International Patent Classification 6 : C08G 63/199, C08J 5/18		A1	(11) International Publication Number: WO 96/06125 (43) International Publication Date: 29 February 1996 (29.02.96)
(21) International Application Number: PCT/US95/10206 (22) International Filing Date: 11 August 1995 (11.08.95) (30) Priority Data: 08/293,627 22 August 1994 (22.08.94) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventor: MILLS, David, Earl; 206 West Central Avenue, Federsburg, MD 21632 (US). (74) Agent: STEVENS, John, F.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: BR, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: BIAXIALLY ORIENTED, HEAT-SET POLYESTER FILM HAVING IMPROVED THERMAL SHRINKAGE RESISTANCE			
(57) Abstract Disclosed is a biaxially stretched, heat-set film having improved resistance to thermal shrinkage and process for producing such film, the film comprising a polyester having repeat units from at least 90 mol % terephthalic acid and at least 90 mol % 1,4-cyclohexanedimethanol wherein the dimensions following biaxial stretching are between 2.0 and 2.5 times the dimensions prior to stretching.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

BIAXIALLY ORIENTED, HEAT-SET POLYESTER FILM HAVING
IMPROVED THERMAL SHRINKAGE RESISTANCE

Technical Field

5 This invention relates to biaxially stretched,
heat-set polyester film of poly(1,4-cyclohexylene-
dimethylene terephthalate) (PCT) with improved thermal
shrinkage resistance and a process for producing the
film. The process conditions described herein produce a
10 film with significantly improved high temperature
dimensional stability.

Background of the Invention

15 It is known in the art that polyester films
sometimes desirably have shrink capability. For
example, it is known in the art that polyester film may
be used as a shrink-wrap material. In such an
application, the film is applied to an object and heated
so that the film shrinks around the object. In the
20 present invention, however, an object is to prepare a
film having shrink resistance. Shrink resistant films
are often used, for example, in various applications
such as flexible electronic circuits, heat resistant
packaging, cooking bags, and any applications requiring
25 dimensional stability at elevated temperatures.

In accordance with the present invention, the
stretch ratio is limited to 2.5X as the maximum for good
shrinkage resistance at high temperatures. This film is
useful for applications requiring a high end use
30 temperature. It is particularly advantageous in
applications requiring a clear, thermally stable film.
Typical end use temperatures for biaxially oriented,
heat-set poly(ethylene terephthalate) (PET) films are
160 to 180°C. The PCT films of this invention can be
35 used at temperatures as high as 250 to 260°C.

- 2 -

An additional desirable property of these films is clarity. If the film is not stretched adequately, haze will be introduced during heat-setting. The lower limit for stretching to produce haze-free films is about 2X in a simultaneous biaxial stretch. There is a process window for stretch ratio that will produce clear, thermally stable PCT film. This window is about 2 to 2.5X stretch for simultaneous biaxial orientation. A sequential stretching mode may change the stretching window.

Because the crystalline melting point and glass transition of PCT are higher than PET, PCT films would be expected to be more thermally stable than PET films. This is not necessarily the case. Subjecting PCT to a film forming process similar to PET where the film is stretched nearly to its breaking point and subsequently heat-set, produces films with poor thermal stability. PCT behaves differently than PET in that once the film is stretched beyond 2.5X, no amount of heat-setting (time or temperature) can anneal the internal stresses generated during the stretching process. With PET, film which is stretched almost to its maximum before breaking can be heat-set to make it thermally stable up to about 200°C. In contrast, PCT cannot be made thermally stable once it is overstretched. The critical process step in this invention addresses this problem.

Oriented PCT films are known to exhibit shrinkage upon heating. Thermal shrinkage limits the end use temperature of the film. For high temperature applications it is desirable to maximize the thermal stability. Heat-setting oriented film increases the temperature at which shrinkage occurs, but if the film is stretched too far, heat-setting does not give thermally stable films. In accordance with this

- 3 -

invention, limiting stretch ratios to 2.5X or less, clear, thermally stable films are produced.

5 Biaxially oriented, heat-set PCT film has been previously disclosed, but using low stretch ratios for improving thermal shrinkage has not been disclosed. Japanese Kokai No. JP1299019 (1980) discloses biaxially stretched, heat-set PCT films with improved dimensional stability, but they did not disclose any examples with stretch ratios less than 3.1X (MD) by 2.8X (TD).

10 U.S. Patent No. 3,284,223 (1966) discloses biaxially oriented, heat-set films of an isophthalic acid modified PCT based copolyester. Although they claimed films from PCT homopolymer, they did not disclose any PCT homopolymer films. Furthermore, their process differed from this invention in that they used a highly asymmetric stretch of 4-5X (MD) by 1-1.25X (TD).

15 Abee and Bell (US Defensive Publication T876,001, July 28, 1970) disclosed a biaxially oriented, heat-set PCT film but no process conditions with less than 3X stretch ratios were disclosed. Likewise, U.S. Patent No. 4,557,982 disclosed films with no stretch ratios less than 3.3X.

In summary, the prior art regarding oriented, heat-set PCT film does not disclose the process conditions of this invention or the shrinkage resistant films of this invention.

25 U.S. Patent No. 2,901,466 discloses in Example 55, films of polyesters from cyclohexanedimethanol, terephthalic acid and isophthalic acid which are stretched in mutually perpendicular direction and heat set. The amount of stretching is not disclosed.

30 U.S. Patent No. 4,994,312 at column 14 discloses stretching film generally in amounts of 1.5-10X, usually 3-4X for polyesters and 6-10 for polypropylene.

- 4 -

Description of the Invention

According to this invention, there is provided a biaxially stretched, heat-set film having improved resistance to thermal shrinkage comprising a polyester
5 having repeat units from at least 90 mol % terephthalic acid and at least 90 mol % 1,4-cyclohexanedimethanol (CHDM) wherein the dimensions following biaxial stretching are between 2.0 and 2.5 times (2.0 and 2.5X) the dimensions prior to stretching.

10 Also, according to this invention, there is provided a method of rendering a polyester film resistant to thermal shrinkage wherein the polyester has repeat units from at least 90 mol % terephthalic acid and at least 90 mol % 1,4-cyclohexanedimethanol, the
15 method comprising biaxially stretching the film to dimensions of 2.0-2.5 times its dimensions prior to stretching, followed by subjecting the film to a temperature of 200 to 280°C, preferably 250 to 280°C, for a time of between 1 and 300 seconds to heat set the
20 film.

The dicarboxylic acid portion of the polyesters and copolyesters from which the repeat units are derived and which are useful in this invention consists essentially of terephthalic acid. The acid portion may be modified
25 with up to about 10 mol % of other acids which may contain 3 to 20 carbon atoms and may consist of units of aromatic, aliphatic, or alicyclic dicarboxylic acids or combinations of these dicarboxylic acids. Examples of useful aliphatic dicarboxylic acids are malonic,
30 succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, 1,4-, 1,5-, and 2,6-decahydronaphthalenedicarboxylic acid, and cis- or trans-1,4-cyclohexanedicarboxylic acid. Examples of useful aromatic dicarboxylic acids are terephthalic
35 acid, isophthalic acid, 4,4'-biphenyldicarboxylic, trans

- 5 -

3,3'- and trans-4,4-stilbenedicarboxylic acid,
4,4'-dibenzoyldicarboxylic acid, 1,4-, 1,5-, 2,3-, 2,6-,
and 2,7-naphthalenedicarboxylic acid.

The cyclohexanedimethanol portion of the
5 copolyester useful in this invention may be replaced
with up to about 10 mol % of other aliphatic glycols,
containing from about 2 to about 10 carbon atoms such as
1,3-propanediol, neopentyl glycol, 1,4-butanediol,
1,5-pentanediol or 1,6-hexanediol.

10 In a preferred embodiment, the cyclohexane
dimethanol component is a cis-/trans-mixture of
1,4-cyclohexanedimethanol.

The polyesters and copolyesters of the present
invention are prepared by conventional polycondensation
15 processes well known in the art, such as the process
described in U.S. Patent 2,901,466 dated August 25,
1959. These include direct condensation of the acid(s)
with the glycol(s) or by ester interchange using lower
alkyl esters.

20 The inherent viscosity of the polyesters or
copolyesters, components (a)-(d), useful in the blends
of the present invention may range from 0.5 to 1.3 dL/g,
a preferred range being 0.6 to 0.8 dL/g, and a more
preferred range being 0.65 to 0.75 dL/g as measured at
25 25°C in a solvent mixture consisting of 60% by weight
phenol and 40% by weight tetrachloroethane.

The reaction is generally begun in the presence of
an excess of the glycol and initially involves heating
to a temperature sufficient to cause a preliminary
30 condensation followed by the evaporation of excess
glycol. The entire reaction is conducted with agitation
under an inert atmosphere. The temperature can then be
advantageously increased with or without the immediate
application of a vacuum.

- 6 -

The 1,4-cyclohexanedimethanol employed can be used in the form of either of its isomers or a mixture thereof. The 1,4-cyclohexanedimethanol or any of the other glycols can be employed as esters thereof (such as
5 esters of a lower alkanolic acid). However, it is generally advantageous to employ the free glycol.

The condensation reaction can be advantageously facilitated by the employment of a catalyst. The best catalyst for each reaction is determined by the nature
10 of the reactants. Generally, when an alkyl ester of the acidic compound is being employed, an ester interchange type of catalyst is to be preferred. Various techniques as to the use of the catalyst are well known in the art. For example, if the free acid is being reacted with the
15 free glycol, a catalyst is generally not added until after the preliminary condensation is under way.

It is sometimes desirable to include any various additives with the polyester mentioned above. There are, for example, titanium dioxide, granulated silica,
20 kaolin, calcium carbonate, and other lubricants; antistatic agents; ultraviolet-light absorbants; pigments; dyes; plasticizers; stabilizers; etc.

The above compositions are formed into a film by any well-known method (such as extrusion, the calendar
25 method, etc.) The shape of the film is not restricted in any way; for example, it can be a flat sheet or a tube.

The stretching method can be by any usual method. As this method, for example, there are the roll
30 stretching method, the long-gap stretching method, the tenter-stretching method, and the tubular stretching method. With use of any of these methods, it is possible to do biaxial stretching in succession, simultaneous biaxial stretching, uniaxial stretching, or
35 a combination of these. With the biaxial stretching

- 7 -

mentioned above, it is possible to do stretching in the machine direction and transverse direction at the same time; or the stretching can be done first in one direction and then in the other direction to result in effective biaxial stretching; stretching can be done first in either direction.

Preferably, in the stretching mentioned above, the following step is then taken. First, for example, the film mentioned above is preliminarily heated at a temperature in the range of a mean glass transition temperature (T_g) of the polymer composition constituting the film to $T_g + 5^\circ\text{C}$ to $T_g + 80^\circ$, preferably $T_g + 10^\circ\text{C}$ to $T_g + 20^\circ\text{C}$.

It is preferred that the stretch rate is 5-20 in./sec. Stretch ratio is defined as the draw ratio in the x-axis direction x the draw ratio in the y-axis direction. The draw ratio is the final length of the film divided by the original length of the film. During the stretching process, the film is not stretched beyond 2.5X in either direction. This process restriction results in film that when subsequently heat-set is shrinkage resistant up to 260°C , depending on heat-setting conditions. Thus, this invention comprises a similar process to that practiced in the art with the provision that the stretch ratio is limited to a maximum of 2.5X in either direction.

The process used to make the PCT films of this invention comprises 1) extruding the polymer into essentially amorphous sheet, 2) stretching the film at a temperature above the polymer glass transition, and 3) heat-setting or annealing the film at a temperature above the desired end use temperature but below the crystalline melting point.

The polymer is extruded into amorphous sheet using methods generally known in the art. The melt

- 8 -

temperature is 300 to 340°C, preferably 305 to 315°C. The roll temperature is 75 to 125°C, preferably 80 to 100°C. The extruded sheet thickness can be in the range of 3 to 60 mil with the actual thickness dependent on the desired end use.

After extrusion, the essentially amorphous sheet is biaxially stretched. The film may be either simultaneously or sequentially stretched in both machine (MD) and transverse (TD) directions. In a simultaneous stretch, the preferred stretch ratio is 2.5X in both directions. In a sequential stretch, either MD or TD may be stretched first with the preferred ratio being 2 to 2.5X for the first stretch and 1.5 to 2.5X for the second stretch. During the stretching process, the film is maintained at a temperature of 105 to 150°C, preferably 110 to 140°C.

After stretching, the film is annealed or heat-set by heating it to a temperature of 180 to 285°C, preferably 240 to 280°C for up to 120 seconds, preferably 2 to 30 seconds. During the heat-setting process, the film dimensions can be held constant or allowed to shrink up to 5 percent.

The following examples are submitted for a better understanding of the invention.

Examples

In the examples, polyester used has repeat units from 100 mol % terephthalic acid and 100 mol % CHDM. The PCT resin had a crystalline melting point of 293°C, a glass transition of 92°C, and an inherent viscosity of 0.80 dl/g. Using a 1 in. Killion extruder with a mixing screw, the polymer is extruded into amorphous sheet with 15 mil thickness. The extrusion die temperature is 300°C and the extrusion roll temperature is 80°C. This amorphous sheet is subjected to various stretching and

- 9 -

heat-setting conditions as described in the following examples. The stretching step is carried out on a T. M. Long machine. Stretching is simultaneous in both machine and transverse directions at a rate of 13 in./sec. Stretched films are clamped in a frame and placed in a forced-air oven for heat-setting.

Thermal shrinkage resistance is measured as tensile heat deflection temperature (HDT) according to ASTM D1637. The test measures the temperature at which 2% deflection occurs under 50 psi stress and does not specify elongation or shrinkage. Except as noted, all deflections reported in these examples as HDT were shrinkage. All HDT measurements are reported as the average of machine direction and transverse direction. Clarity is measured either as transparency according to ASTM D1746 or as haze according to ASTM D1003.

1. PCT film is stretched 2X by 2X at 130°C using a preheat time of 45 sec. After heat-setting at 250°C for 2 min, the biaxially oriented, heat-set PCT film has an HDT of 234°C.
2. PCT film is stretched 2.5X by 2.5X at 130°C using a preheat time of 45 sec. After heat-setting at 280°C for 2 min, the biaxially oriented, heat-set PCT film has an HDT of 265°C.
3. PCT film is stretched 2.5X by 2.5X at 130°C using a preheat time of 45 sec. After heat-setting at 250°C for 2 min, the biaxially oriented, heat-set PCT film has an HDT of 235°C and 1.3% haze.

- 10 -

Comparative Examples

5. Poly(ethylene terephthalate) (PET) film is stretched 3X by 3X at 100°C using a preheat time of 45 sec. After heat-setting at 240°C for 2 min, the biaxially oriented, heat-set PET film has an HDT of 217°C and 0.7% haze.
6. PCT film is stretched 3X by 3X at 110°C using a preheat time of 45 sec. After heat-setting in two stages at 150°C for 2 min, followed by 200°C for 2 min the biaxially oriented, heat-set PCT film has an HDT of 140°C and 88% transparency.
7. PCT film is stretched 3X by 3X at 110°C using a preheat time of 45 sec. After heat-setting in two stages at 150°C for 2 min, followed by 250°C for 2 min the biaxially oriented, heat-set PCT film has an HDT of 168°C and 87% transparency.
8. PCT film is stretched 3X by 3X at 130°C using a preheat time of 45 sec. After heat-setting at 250°C for 2 min, the biaxially oriented, heat-set PCT film has an HDT of 175°C and 85% transparency.
9. PET film is stretched 2X by 2X at 100°C using a preheat time of 45 sec. After heat-setting at 220°C for 2 min, the biaxially oriented, heat-set PET film has an HDT of 195°C.

- 11 -

Table 1

Summary of Examples and Comparative Examples

		<u>Stretch Ratio</u>	<u>Stretch Temp (°C)</u>	<u>Heat-set Temp (°C)</u>	<u>HDT (°C)</u>
5	Examples:				
10	1	2	130	250	234
	2	2.5	130	280	265
	3	2.5	130	250	235
15	Comparative Examples:				
	5 (PET)	3	100	240	217
20	6	3	110	200	140
	7	3	110	250	168
25	8	3	130	250	175
	9 (PET)	2	100	220	195

The designation "X" as used herein, such as 2X and 2.5X, means the film is stretched that many times its dimensions prior to stretching. For example, 2X means that the film is stretched to a final elongation of 100%. The film dimension in the stretching direction doubles in a 2X stretch.

The data in Table 1 clearly indicate that the process of this invention produces films with superior heat resistance. Comparing Examples 1 and 3 with Example 8 shows that films produced with a stretch ratio of 2.5X or less have unexpectedly high HDT compared with film stretched 3X. These data also show the superior properties of the PCT films of this invention as compared to PET films which are well known in the art.

- 12 -

I.V. herein is measured at 25°C using 0.50 g of polymer per 100 mL of a solvent consisting of 60 wt % phenol and 40 wt % tetrachloroethane.

5 This invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

- 13 -

CLAIMS

I claim:

- 5 1. A biaxially stretched, heat-set film having improved resistance to thermal shrinkage comprising a polyester having repeat units from at least 90 mol % terephthalic acid and at least 90 mol %
10 1,4-cyclohexanedimethanol characterized by the dimensions following biaxial stretching being between 2.0 and 2.5 times the dimensions prior to stretching.
- 15 2. A film according to Claim 1 wherein the I.V. of the polyester is 0.5 to 1.3 dL/g.
- 20 3. A film according to Claim 1 wherein the cyclohexanedimethanol is a mixture of cis- and trans-1,4-cyclohexanedimethanol.
- 25 4. The method of rendering a polyester film resistant to thermal shrinkage wherein said polyester has repeat units from at least 90 mol % terephthalic acid and at least 90 mol % 1,4-cyclohexane-
30 dimethanol, said method characterized by biaxially stretching said film to dimensions of 2.0-2.5 times its dimensions prior to stretching, followed by subjecting said film to a temperature of about 200 to about 280°C for a time of between 1 and 300 seconds to heat set said film.

INTERNATIONAL SEARCH REPORT

Intern. al Application No

PCT/US 95/10206

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/199 C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 14771 (EASTMAN KODAK CO.) 3 September 1992 see claims 1-3,10-12 ---	1-4
A	EP,A,0 483 757 (DIAFOIL CO. LTD) 6 May 1992 see claim 1; example 1 see page 3, line 56 - page 4, line 8 --- <i>5, 153, 302</i>	1-4
A	EP,A,0 402 861 (DIAFOIL CO. LTD.) 19 December 1990 see page 3, line 44 - page 4, line 13 ---	4
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 90-271569(36) & JP,A,2 191 638 (UNITIKA KK) 27 July 1990 see abstract --- -/-	1-4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

28 November 1995

Date of mailing of the international search report

29.12.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

O'Sullivan, T

INTERNATIONAL SEARCH REPORT

Intern: a) Application No
PCT/US 95/10206

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Derwent Publications Ltd., London, GB; AN 82-82365E(39) & JP,A,57 135 118 (TEIJIN KK) 20 August 1982 see abstract</p> <p>-----</p>	1-4

Form PCT/ISA/218 (continuation of second sheet) (July 1992)

page 2 of 2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/10206

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9214771	03-09-92	NONE	
EP-A-0483757	06-05-92	JP-A- 4164627	10-06-92
		JP-B- 6059686	10-08-94
		DE-D- 69110616	27-07-95
		US-A- 5153302	06-10-92
EP-A-0402861	19-12-90	JP-A- 3013315	22-01-91
		JP-A- 3024936	01-02-91
		DE-D- 69008425	01-06-94
		DE-T- 69008425	01-12-94
		US-A- 5093064	03-03-92
		US-E- RE34727	13-09-94

Form PCT/ISA/210 (patent family annex) (July 1992)